Available online at www.sciencedirect.com

ScienceDirect

Dyes and Pigments 77 (2008) 493–501

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Electroreduction and spectrophotometric studies of some pyrazolyl-azo dyes derived from 3-acetylamino-1-phenyl-5-pyrazolone in buffered solutions

M.M. Ghoneim*, H.S. El-Desoky, S.A. Amer, H.F. Rizk, A.D. Habazy

Electrochemistry Research Unit, Chemistry Department, Faculty of Science, Tanta University, 31527 Tanta, Egypt

Received 27 May 2007; received in revised form 30 July 2007; accepted 31 July 2007
Available online 10 August 2007

Abstract

Four pyrazolyl-azo dyes derived from 3-acetylamino-1-phenyl-5-pyrazolone were prepared and characterized. The electroreduction of the prepared azo dyes was studied at a mercury electrode in the universal buffer at pH 2–12.2 containing 10% DMF using dc-polarography, cyclic voltammetry and controlled-potential coulometry. The dc-polarograms of the examined pyrazolyl-azo dyes (I–IV) exhibited a single 4-electron irreversible cathodic wave in solutions of pH values: <7, <9.4, <10.5, and <9.4, respectively, which can be attributed to reduction of the N=N– group of the dye to the corresponding amine via the consumption of four electrons. Increase of pH resulted in the reduction wave splitting into two, the limiting current of the 2nd wave increasing at the expense of the first until the latter disappeared completely in solutions of pH ≥9.5 (I), ≥11.2 (II) and ≥12.2 (III and IV). This behavior indicated that both the acidic and basic forms of the azo dye molecule were electroactive at the mercury electrode. The ionization constants (pK_a) of the dyes were determined by means of dc-polarographic and spectrophotometric measurements. The electrode reaction pathway of the studied compounds was elucidated and discussed.

Keywords: Pyrazolyl-azo dyes; Electroreduction; Diffusion coefficient; Spectrophotometry; Ionization constant

1. Introduction

The widespread applications of the azo dyes as chromophoric and metallochromic reagents [1–5], photochromic materials [6,7], colorants [8–15], non-linear optics [16–21], photo-sensitizers [22–24] and sensors [25–28] have attracted the interest of many electrochemists [29–42]. The reported electrochemical results showed that the electroreduction of the N=N double bond took place to the hydrazo stage (HN–NH) via the consumption of $2e^-/2H^+$ or to the amine stage ($-NH_2$) via the consumption of $4e^-/4H^+$ in one or two steps depending on the chemical structure of the investigated azo dye compound, nature of neighboring substituents and pH of the electrolyzed medium. In this work a systematic study was undertaken to investigate the electroreduction of some pyrazolyl-azo dyes derived from 3-acetylamino-1-phenyl-5-pyrazolone at the mercury electrode and to elucidate their electrode reaction pathway using different electrochemical techniques. Besides, the ionization constant of each of the investigated azo dyes was estimated by means of electrochemical and spectrophotometric measurements.

2. Experimental

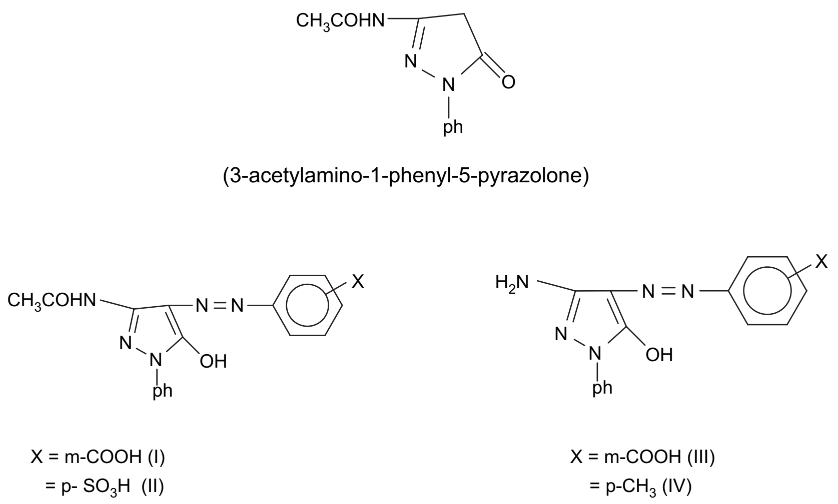
2.1. Pyrazolyl-azo dyes

Four pyrazolyl-azo dyes I–IV (Scheme 1) were prepared by the reaction of 3-acetylamino-1-phenyl-5-pyrazolone with *m*-carboxybenzene diazonium chloride and *p*-sulphoxy-benzene diazonium chloride in pyridine to form the corresponding azo dyes [43–45]. The obtained pyrazolyl-azo dyes were 3-[3-(acetylamino)-5-hydroxy-1-phenyl-4-pyrazolyl-azo]benzoic

---

* Corresponding author. Tel.: +2 010 6632694; fax: +2 040 3350804.
E-mail address: mmghoneim@usa.net (M.M. Ghoneim).

0143-7208/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2007.07.018



Scheme 1. Structure of the investigated pyrazolyl-azo dyes.

acid (I), 4-[3-(acetylamino)-5-hydroxy-1-phenyl-4-pyrazolyl-azo] benzene sulphonic acid (II), 3-[3-amino-5-hydroxy-1-phenyl-4-pyrazolyl-azo]benzoic acid (III) and 4-[3-amino-5-hydroxy-1-phenyl-4-pyrazolyl-azo]toluene (IV).

Purity of the prepared pyrazolyl-azo dyes was ascertained by recrystallization from pure ethanol. The chemical structures of the prepared pyrazolyl-azo dyes were confirmed by elemental analysis, ^{1}H NMR and MS-spectral investigations (Table 1).

2.2. Solutions

Standard stock solutions of 1×10^{-3} M of each of the prepared pyrazolyl-azo dyes (I–IV) were prepared by dissolving the appropriate amount of the solid compound in a suitable volume of absolute dimethylformamide (Merck). A series of the Britton–Robinson (B–R) universal buffer of pH values 2–12 was prepared [46] and used as a supporting electrolyte. A pH-meter (Crison, Barcelona, Spain) was used for the pH measurements.

2.3. Instrumentation

A Sargent-Welch polarograph model 4001 (Fisher, USA) was used for the polarographic measurements. The electrolysis cell used was as described by Mietes [47]. The characteristics of the capillary used as a dropping mercury electrode (DME) was $m = 1.72$ mg/s and $t = 3$ s in a solution of 0.1 M KCl at open circuit conditions for a mercury height of 60 cm. A saturated calomel electrode (SCE) was used as a reference electrode.

Computer-controlled electrochemical analyzer model 273A–PAR (Princeton Applied Research, Oak Ridge, TN, USA) and the electrode assembly model 303A, incorporated with a micro-electrolysis cell and a three electrode configuration system comprising of a hanging mercury drop electrode (HMDE) as a working electrode (surface area = 0.026 cm^2), an Ag/AgCl/KCl$_s$ reference electrode and a platinum wire auxiliary electrode was used for the cyclic voltammetric measurements.

Table 1
Elemental analysis, ^{1}H NMR and mass spectroscopic data of the prepared pyrazolyl-azo dyes

Comp. (mol. wt.)	Mp.°C	Elemental analysis (%) calculated/found				^{1}H NMR (δ in ppm) and mass spectra
		C	H	N	S	
I						
$C_{18}H_{15}N_5O_4$ (365.34)	270.3	59.18	4.14	19.17	–	δ/ppm = 2.5 (s, 3H, CH_3), 6.5 (s, 1H, NH), 7.3–8.5 (m, 9H, ArH), 11.0 (s, 1H, COOH); MS = 365 $M^{\surd+}$, 323 (100%)
		59.08	4.09	19.09	–	
II						
$C_{17}H_{15}N_5O_5S$ (401.4)	220.2	50.87	3.77	17.45	7.99	δ/ppm = 2.8 (s, 1H, SO_3H), 2.5 (s, 3H, CH_3), 6.5 (s, 1H, NH), 7.3–8.2 (m, 9H, ArH); MS = 402 $M^{\surd+}$, 277 (100%)
		50.78	3.65	17.39	7.90	
III						
$C_{16}H_{13}N_5O_3$ (323.31)	292.3	59.44	4.05	21.66	–	δ/ppm = 4 (s, 2H, NH_2), 7.3–8.5 (m, 9H, ArH), 11.0 (s, 1H, COOH); MS = 322 $M^{\surd+}$ (100%)
		59.39	3.98	21.60	–	
IV						
$C_{16}H_{15}N_5O$ (293.32)	>350	65.52	5.15	23.88	–	δ/ppm = 3.1 (s, 3H, CH_3), 4 (s, 2H, NH_2), 7.3–8.2 (m, 9H, ArH); MS = 335 $M^{\surd+}$ (100%)
		65.48	5.09	23.81	–	

A potentiostat/galvanostat (model 173-PAR) incorporated with a digital coulometer model 179-PAR were used for controlled-potential electrolysis of the investigated pyrazolyl-azo dyes at a mercury pool as a working electrode. A saturated calomel electrode as a reference and a platinum gauze immersed in a bridge tube as a counter electrode were used. The potential selected was adjusted to a value equal to the $E_{1/2}$ of the polarographic wave of reactant plus -0.1 V or at the beginning of the limiting current of the polarographic wave. The electrolyzed solutions were deoxygenated before measurements by bubbling pure nitrogen while a stream of nitrogen gas was kept over surface of the electrolysis solution during the measurements. The number of electrons (n) transferred per azo-molecule was determined using Faraday's relation: $N = Q/nF$ (where N is the number of moles of substance being electrolyzed) and was found to equal four electrons per molecule of the examined azo dye (I–IV). The positive azo test for the completely electrolyzed solutions of the examined azo dyes confirmed the reductive cleavage of the –N═N– double bond.

Electronic absorption spectra of the pyrazolyl-azo dyes under consideration in Britton–Robinson universal buffer of pH values 2–12 were recorded at room temperature within the wavelength range 200–600 nm using a Shimadzu UV–visible spectrophotometer model 160A.

3. Results and discussion

3.1. dc-Polarographic studies

Polarograms of each of the examined pyrazolyl-azo dyes I–IV exhibited a single 4-electron irreversible cathodic wave in the Britton–Robinson universal buffer of the pH values <7, <9.4, <10.5 and <9.4, respectively (e.g. Fig. 1). This behavior may be attributed to the reduction of the azo –N═N– center to the corresponding amine via the consumption of four electrons per azo dye molecule. On increasing pH of the medium, the reduction wave of each of the examined azo dyes splits into two waves, the limiting current of the second wave increased at the expense of the first one until the latter disappeared completely in solutions of the pH values ≥9.5, ≥11.2 and ≥12.5, respectively, for the pyrazolyl-azo dyes (I), (II) and (III and IV) where the polarograms exhibited a single four electron wave at more negative potentials (e.g. Fig. 1). The cumulative i_l–pH curve for the single wave and the 1st splitting one (e.g. Fig. 3, curve a) and that for the 2nd splitting wave and the single wave at more negative potentials (e.g. Fig. 2, curve b) recalled, respectively, dissociation (Z-shaped) and association (S-shaped) curves, a behavior that may be attributed to the presence of the investigated azo dye molecule in an acid–base equilibrium [48]. The two cumulative i_l–pH curves for each of the investigated azo dyes were intersected (e.g. Fig. 2, curves a and b) at the pH values, 7.5, 9.7, 11.1 and 9.7 which are equal, respectively, to the pK_a values of the investigated azo dyes I–IV. The obtained pK_a values of the investigated pyrazolyl-azo dyes (Table 2) are in good accordance with those obtained by means of spectrophotometric methods (Table 2). The limiting current (i_l) of each of the reduction waves of the investigated azo dyes was proportional to the square root of the mercury height (h). Plots of log (i_l) versus log (h) for the investigated azo dyes at the various pH values were straight lines with slope values amounting to 0.5–0.6 indicating that the reduction processes of the investigated pyrazolyl-azo dyes at the mercury electrode are mainly controlled by diffusion [47].

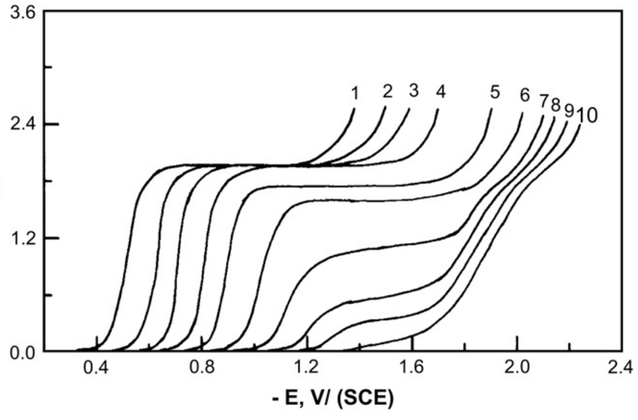


Fig. 1. dc-Polarograms for 2.5×10^{-4} M of the pyrazolyl-azo dye (IV) in the B–R universal buffer of various pH values containing 10% (v/v) DMF: (1) 3.2, (2) 4.2, (3) 4.9, (4) 6, (5) 7, (6) 8.2, (7) 9.4, (8) 10, (9) 11, and (10) 12.2.

The reduction waves of the pyrazolyl-azo dyes under consideration were analyzed using the fundamental equation for irreversible polarographic waves [47]:

$$E_{\mathrm{d.e.}} = E_{1/2} - (59/\alpha n_a)\log(i/i_l - i) \qquad (1)$$

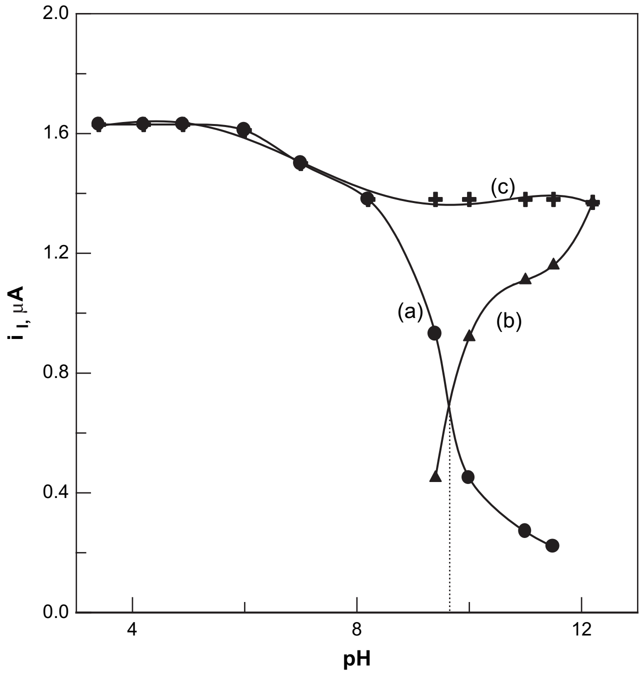


Fig. 2. i_l–pH plots for 2.5×10^{-4} M of the pyrazolyl-azo dye (IV). (a) The single wave (pH < 9.4) and the 1st splitting wave (pH 9.4–11.5); (b) the 2nd splitting wave (pH 9.4–11.5) and the single wave (pH ≥ 12.2) and (c) the total limiting current.

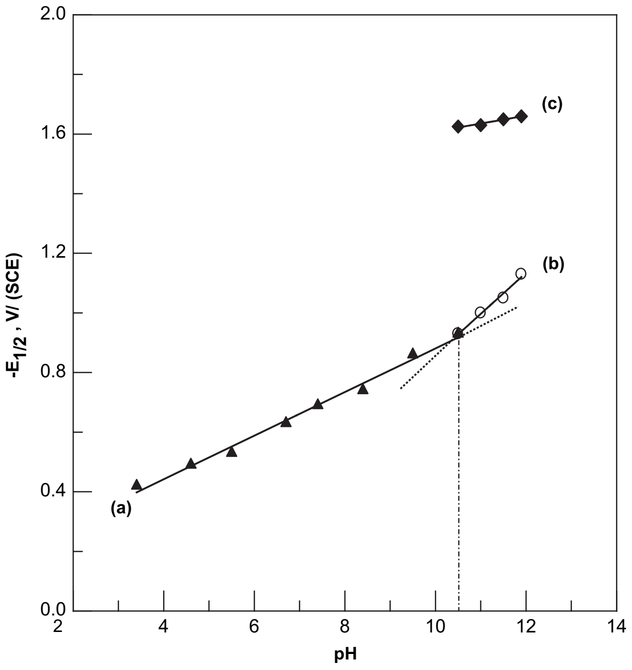


Fig. 3. $E_{1/2}$–pH plots for 2.5×10^{-4} M of the pyrazolyl-azo dye (III). (a) The single wave (pH < 10.5), (b) the 1st splitting wave (pH 10.5–11.9), (c) the 2nd splitting wave (pH 10.5–11.9) and the single wave (pH ≥ 12.2).

Table 3
dc-Polarographic results of the investigated pyrazolyl-azo dyes in the B–R universal buffer of various pH values, at 25 °C

Azo dye	pH	S_1 (mV)	αn_a	α $n_a = 2$	S_2 (mV)	α Z_{H}^{+}/n_a			Z_{H}^{+} (S_2/S_1)
						2	1	0.5	
I	4.0	45	1.31	0.65	50	2.81	1.18	0.59	1.1
	7.0[a]	45	1.31	0.65	45	2.62	1.31	0.65	1.0
	7.0[b]	60	0.98	0.49	–	–	–	–	–
	12.0	55	1.07	0.53	–	–	–	–	–
II	4.4	103	0.57	0.29	107	1.10	0.55	0.28	1.0
	10.1[a]	95	0.62	0.31	85	1.39	0.69	0.35	0.9
	10.1[b]	101	0.58	0.29	–	–	–	–	–
	11.2	100	0.59	0.30	–	–	–	–	–
III	4.3	74	0.80	0.40	72	1.64	0.82	0.41	1.0
	10.5[a]	88	0.67	0.33	100	1.18	0.59	0.30	1.1
	10.5[b]	80	0.74	0.37	–	–	–	–	–
	12.2	86	0.68	0.34	–	–	–	–	–
IV	4.2	60	0.98	0.49	70	1.69	0.84	0.42	1.2
	10.0[a]	60	0.98	0.49	62	1.90	0.95	0.47	1.0
	10.0[b]	58	1.02	0.51	–	–	–	–	–
	12.2	86	0.68	0.34	–	–	–	–	–

[a] 1st splitting wave.
[b] 2nd splitting wave.

Plots of $E_{\mathrm{d.e}}$ versus log $(i/i_1 - i)$ for the investigated azo dyes at the various pH values were straight lines with the slope values S_1, ($S_1 = 59/\alpha n_a$) reported in Table 3, from which values of αn_a and the symmetry transfer coefficient α were estimated considering the number of electrons (n_a) involved in the rate-determining step equals 1 or 2. The most probable values of the α-parameter over the entire pH range revealed that n_a equals two. The obtained α-values (Table 3) confirmed the irreversible nature of the reduction processes of the investigated pyrazolyl-azo dyes.

The half-wave potentials ($E_{1/2}$) of the single reduction wave of each of the investigated azo dyes (I–IV) recorded, respectively, in solutions of the pH values <7, <9.4, <10.5 and <9.4, and those of the first splitting waves recorded in solutions of higher pH values were shifted toward more negative values with the increase of pH (e.g. Fig. 3 – curves a and b) indicating the involvement of protons in the rate-determining step of the reduction processes of the investigated pyrazolyl-azo dyes and that the proton transfer precedes the electron transfer reaction [48]. While the $E_{1/2}$ of both the second splitting waves and the single waves at the pH values ≥9.5, ≥11.2 and ≥12.2, respectively, for the examined azo dyes I, II and (III and IV) were practically pH-independent (e.g. Fig. 3 – curve c). The linear $E_{1/2}$–pH plots for the main single wave and that for the 1st splitting one of each of the investigated azo dyes were intersected at a pH value equal to the pK_a value of the investigated azo dye (e.g. Fig. 3, curves a and b). The estimated pK_a values for the investigated azo dyes (I–IV) are in good accordance with those obtained from the i_1–pH curves of the investigated pyrazolyl-azo dyes (Table 3).

Table 2
Values of the pK_a of the investigated pyrazolyl-azo dyes as determined by electrochemical methods: {(a) i_1–pH curves, (b) $E_{1/2}$–pH curves and (c) log $[(i_1 - i_{\mathrm{HA}})/i_{\mathrm{HA}}]$ and log $[(i_1 - i_{\mathrm{A}}^{-})/i_{\mathrm{A}}^{-}]$–pH curves} and spectrophotometric methods: {(d) absorbance–pH curves, (e) the half-height and (f) the modified limiting absorbance methods}

Azo dye	pK_a					
	Electrochemical methods			Spectrophotometric methods		
	(a)	(b)	(c)	(d)	(e)	(f)
I	7.5	7.0	7.5	7.4	7.5	7.7
II	9.7	9.4	9.7	9.8	9.5	9.3
III	11.1	10.5	11.1	11.4	11.2	11.0
IV	9.7	10.0	9.7	9.8	9.2	9.9

From the slope values S_2, {$S_2 = (59/\alpha n_a)\, Z_{\mathrm{H}}^{+}$} of the $E_{1/2}$–pH plots of the main single waves and that of the 1st splitting waves (e.g. Fig. 3, curves a and b) of each of the investigated azo dyes, the number of hydrogen ions (Z_{H}^{+}) participating in the rate-determining step of the reduction process of each of the investigated azo dyes was determined using Eq. (2) [47,49]:

$$Z_{\mathrm{H}}^{+} = (\delta E_{1/2}/\delta \mathrm{pH})/(59/\alpha n_a) = S_2/S_1 \tag{2}$$

and was found to equal one (Table 3). Furthermore, values of the symmetry transfer coefficient (α) were determined at different ratios of (Z_{H}^{+}/n_a) using Eq. (3) [47]:

$$\alpha = 59/S_2(Z_{\mathrm{H}}^{+}/n_a) \tag{3}$$

where the ratio (Z_{H}^{+}/n_a) can have value of 2, 1 or 0.5 depending on whether one or two electrons and one or two protons are involved in the rate-determining step. From the data given in

Table 3, the most probable values of the α-parameter for all the investigated pyrazolyl-azo dyes denoted that the ratio $(Z_{\mathrm{H}}^{+}/n_{\mathrm{a}}) = 0.5$ which meant that the rate-determining step of the reduction process of each of the investigated pyrazolyl-azo dyes may involve one proton and two electrons. (i.e. $Z_{\mathrm{H}}^{+} = 1$ and $n_{\mathrm{a}} = 2$).

The diffusion coefficients D^0 of the investigated pyrazolyl-azo dyes were estimated from their limiting current obtained in acidic and basic media by means of Ilkovic equation [50] and the obtained values are reported in Table 4. The results shown in Table 4 indicated that value of the diffusion coefficient (D^0) of the reducible species decreased with the increase of molecular weight of the investigated azo dyes. On the other side, value of D^0 decreased on increasing pH of the medium from pH 4 to pH 12 which may be attributed to the increased viscosity of the electrolysis medium.

3.2. Cyclic voltammetric studies

Cyclic voltammograms of the investigated pyrazolyl-azo dyes (I–IV) at the HMDE recorded in the B–R universal buffer of various pH values containing 10% (v/v) DMF at various scan rates (50–500 mV/s) exhibited the same behavior obtained by dc-polarographic measurements (e.g. Fig. 4). The irreversible nature of the reduction processes of the examined pyrazolyl-azo dyes was confirmed from the shift of the peak potentials (E_{p}) to more negative values on increasing the scan rate v (e.g. Fig. 4). The E_{p} versus ln v plots for the investigated azo dyes at various pH values were straight lines with slope values proportional to αn_{a} [51]. Values of the symmetry transfer coefficient α of 0.43–0.71 were obtained which again confirmed the irreversible nature of the reduction processes of the investigated azo dyes. On plotting i_{p} versus square root of the scan rate ($v^{1/2}$) [52] for the investigated pyrazolyl-azo dyes, linear correlations were obtained which confirmed that the electrode processes of the investigated azo dyes are mainly controlled by diffusion [53].

3.3. Controlled-potential coulometry studies

In order to verify the overall number of electrons consumed in the reduction process, solutions of the investigated pyrazolyl-azo dyes were electrolyzed at a controlled-potential of −0.1 V more cathodic than the $E_{1/2}$ of the examined azo dye at the various pH values. The results obtained revealed that the total number of electrons (n) involved in the overall reduction process of each of the examined azo dyes (I–IV) are four electrons per azo dye molecule over the entire pH

Table 4
Diffusion coefficient of the investigated pyrazolyl-azo dyes as calculated by means of the Ilkovic equation ($C = 0.25$ mM, $m = 1.72$ mg s^{-1} and $t = 3$ s) in B–R universal buffer of acidic and alkaline pH values at 25 °C

Azo dye	Molecular weight (g)	D^0 (cm^2/s)	
		pH 4	pH 12
I	365.34	2.05×10^{-6}	1.43×10^{-6}
II	401.40	1.05×10^{-6}	7.40×10^{-7}
III	323.31	2.11×10^{-6}	1.54×10^{-6}
IV	293.32	2.43×10^{-6}	1.70×10^{-6}

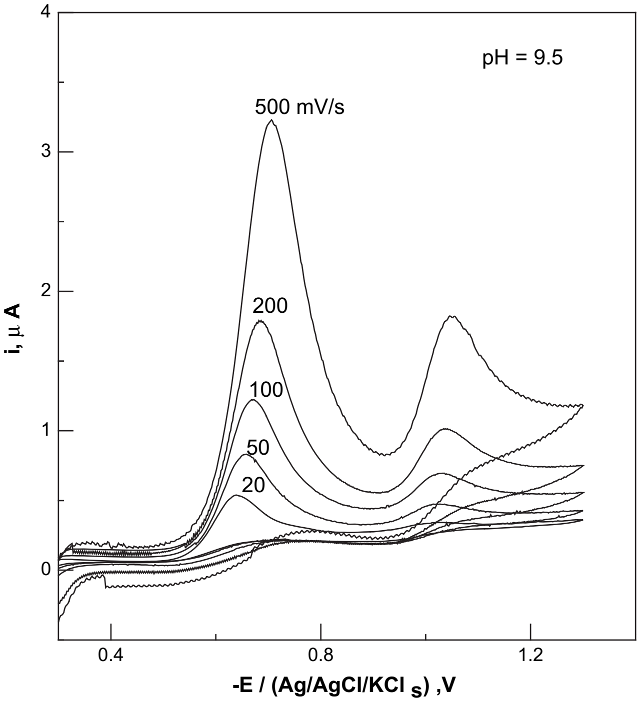


Fig. 4. Cyclic voltammograms for 1×10^{-4} M of the pyrazolyl-azo dye (III) in the B–R universal buffer of pH 9.5 containing 10% (v/v) DMF at different scan rates.

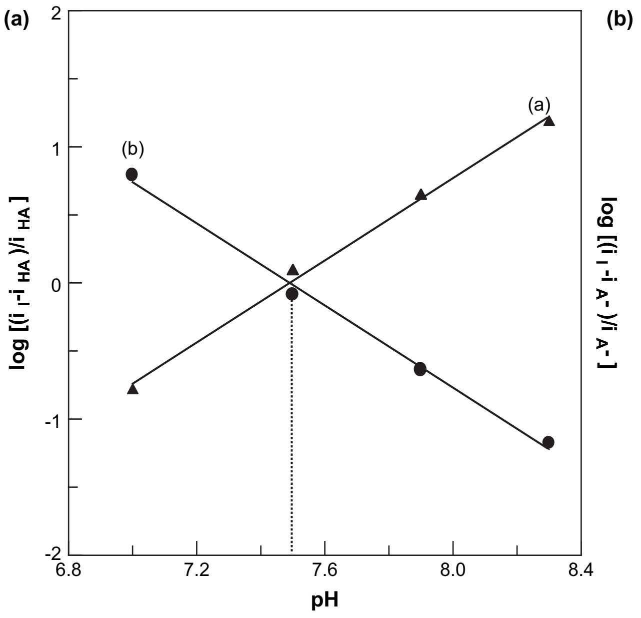


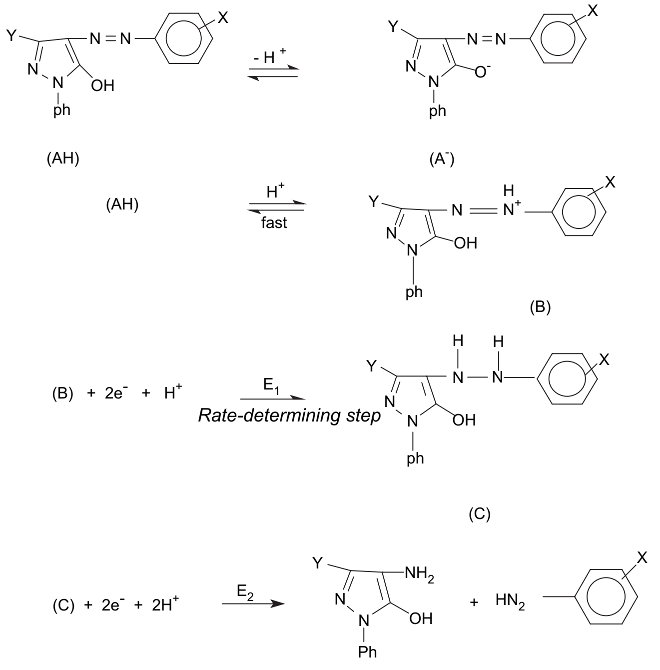
Fig. 5. Plots of $\log[(i_{\mathrm{l}} - i_{\mathrm{HA}})/i_{\mathrm{HA}}]$ or $\log[(i_{\mathrm{l}} - i_{\mathrm{A}^-})/i_{\mathrm{A}^-}]$ versus pH for 2.5×10^{-4} M of the pyrazolyl-azo dye (I): (a) 1st splitting wave and (b) 2nd splitting wave recorded in solutions of pH 7.0–8.3.

range which were consumed for the reductive cleavage of the N=N double bond (Schemes 2 and 3). The positive azo test for the completely electrolyzed solutions of the investigated azo dyes was a clear evidence for the reductive cleavage of the −N=N− center at the mercury electrode to the amine stage.

3.4. The electrode reaction

Considering the foregoing results and those previously reported for the electrochemical behavior of various azo dyes [29,31–33,38–41] based on the reduction of the N=N double bond via the consumption of four electrons over the entire pH range, the electroreduction reaction pathway of the examined pyrazolyl-azo dyes at the mercury electrode can be expressed as follows:

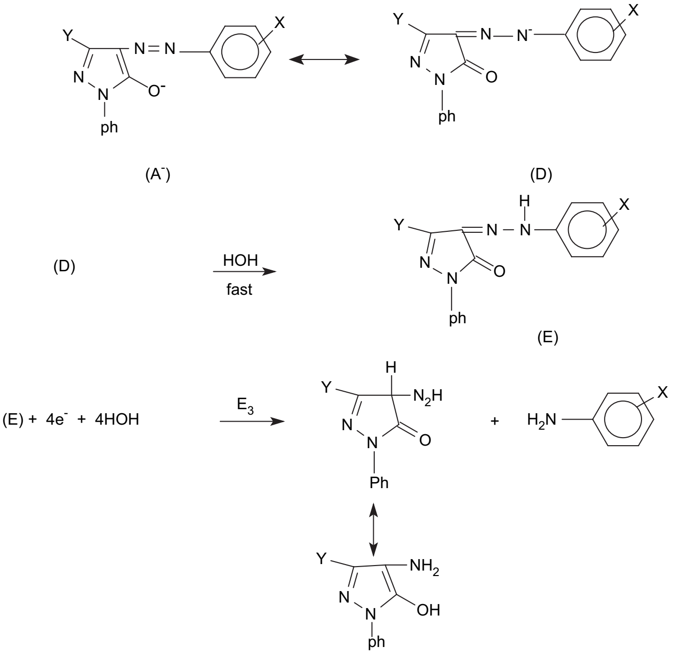
(i) In solutions of pH value < 7 (I), <9.4 (II), <10.5 (III) or <9.4 (IV), where the pyrazolyl-azo dyes are considered to be present in the acidic form species (AH), the electrode reaction pathway can be expressed in Scheme 2:



Scheme 2

where $E_1 = E_2 = E_{1/2}$ of the single 4-electron reduction step took place in the solutions of the indicated pH values.

(ii) In alkaline solutions of pH values ≥9.5 (I), ≥11.2 (II) or ≥12.2 (III and IV), where the pyrazolyl-azo dyes are considered to be present in the basic form species (A^-), the electrode reaction pathway can be expressed as follows:



Scheme 3

where $E_3 = E_{1/2}$ of the single 4-electron reduction step took place in the alkaline solutions of the indicated pH values.

(iii) In solutions of the intermediate pH values: 7–8.3 (I), 9.4–10.9 (II), 10.5–11.9 (III) and 9.4–11.5 (IV), each of the considered pyrazolyl-azo dyes is present in an acid–base equilibrium which can be expressed as:

$$AH \underset{k_r}{\overset{k_d}{\rightleftharpoons}} A^- + H^+ \quad \left(K = k_d/k_r\right)$$

where both the acidic (AH) and basic (A^-) forms are electro-active at the mercury electrode. Thus, the reduction of the investigated pyrazolyl-azo dyes within the intermediate pH ranges took place via two steps. The limiting current of the second step (which corresponds to the reduction of the −N=N− center of the basic species A^-) increased at the expense of the first one (which corresponds to the reduction of the −N=N− center of the acidic species AH) on increasing pH of the medium until the latter one disappeared completely at pH values ≥ 9.5 (I) ≥ 11.2 (II) and ≥ 12.2 (III and IV). Thus, the electrode reaction of the investigated pyrazolyl-azo dyes over the indicated intermediate pH values may be considered to consist of a mixture of the two processes (i) and (ii).

According to Zuman [48], the existence of an electro-active compound in an acid–base equilibrium leads to variation of its reduction current with the change of hydrogen ion concentration $[H^+]$ as governed by Eq. (4):

$$\frac{i_{AH}}{i_l} = \frac{0.886\left\{(k_r t_l)[H^+]\right\}^{1/2}}{1 + 0.886\left\{\left(\frac{k_r t_l}{K}\right)[H^+]\right\}^{1/2}} \tag{4}$$

which was modified to the following forms [48,54]:

$$\mathrm{pH} = \log 0.886\left(\frac{k_{\mathrm{r}}t_{1}}{K}\right)^{1/2} + \log\left(\frac{i_{1} - i_{\mathrm{AH}}}{i_{\mathrm{AH}}}\right) \tag{5}$$

$$\mathrm{pH} = \log 0.886\left(\frac{k_{\mathrm{r}}t_{1}}{K}\right)^{1/2} + \log\left(\frac{i_{1} - i_{\mathrm{A}}^{-}}{i_{\mathrm{A}}^{-}}\right) \tag{6}$$

(i_{AH} and i_{A}^{-} are the reduction currents of acidic and basic forms, respectively). The plots of [$\log(i_{1} - i_{\mathrm{AH}})/i_{\mathrm{AH}}$] or [log-$(i_{1} - i_{\mathrm{A}}^{-})/i_{\mathrm{A}}^{-}$] versus pH, respectively, for the 1st splitting and the 2nd splitting waves of the investigated pyrazolyl-azo dyes were straight lines (e.g. Fig. 5, curves a and b) indicating the validity of the previous equations and consequently confirmed the presence of the pyrazolyl-azo dye molecule in an acid–base equilibrium within the intermediate pH range. The pH value corresponds to the intersection point of the two curves of each of the investigated compounds equals its pK_{a} value. The obtained pK_{a} values of the examined pyrazolyl-azo dyes are reported in Table 2.

3.5. Substituents' effect

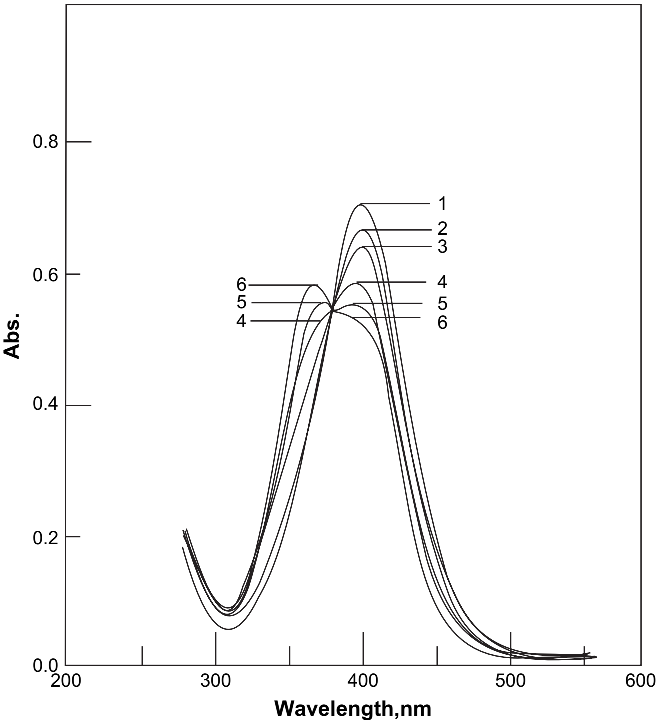


Fig. 6. Absorption spectra of 4×10^{-5} M of the pyrazolyl-azo dye (IV) in the B–R universal buffer of various pH values containing 10% (v/v) DMF: (1) pH 3.1, (2) 5.6, (3) 7.8, (4) 9, (5) 9.8 and (6) 10.7.

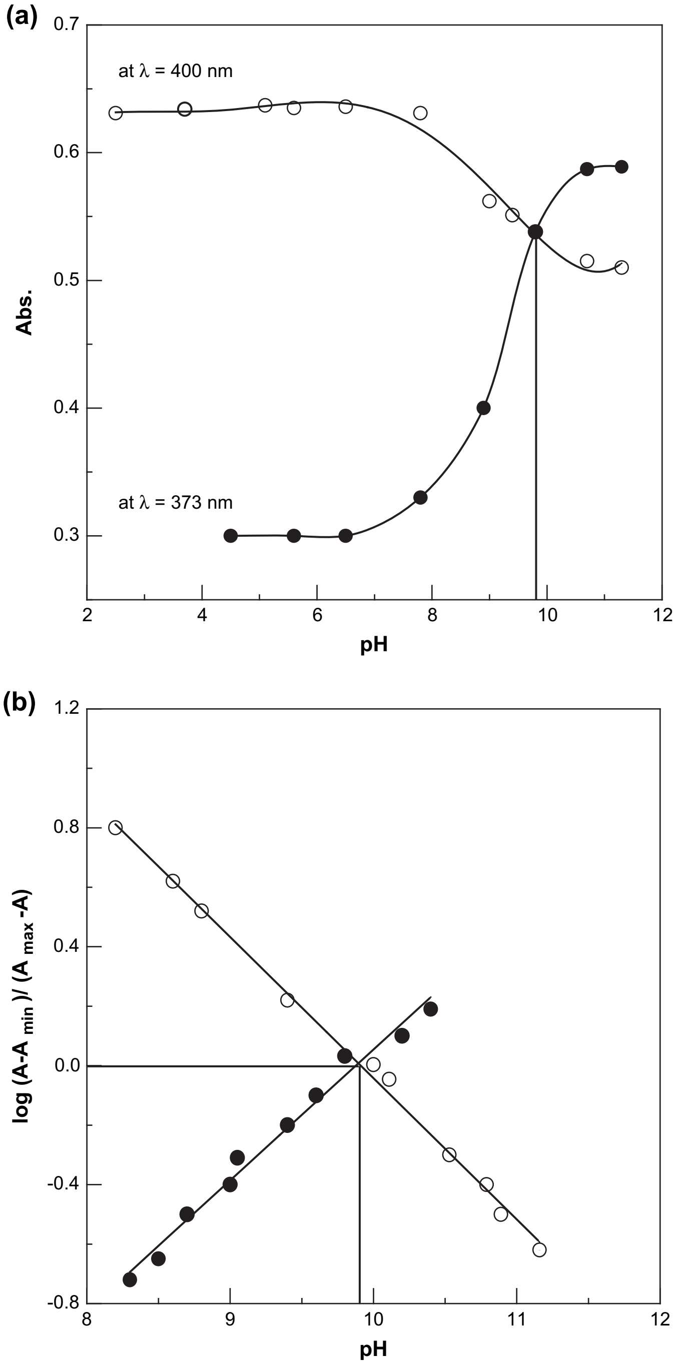


Fig. 7. Plots of absorbance–pH (a) and {log $(A - A_{\mathrm{min.}})/(A_{\mathrm{max}} - A)$–pH} (b) for the pyrazolyl-azo dye (IV) in the B–R universal buffer.

The substituents' effect on the reduction process of the investigated pyrazolyl-azo dyes was identified by applying the Hammett equation [55]. A practically linear plot of $E_{1/2}$ (of the 1st polarographic wave of the investigated compounds in a B–R buffer of pH 5) versus the Hammett constants (σ_x) was obtained with a slope (ρ_π) of 0.27. The positive value of the specific rate constant (ρ_π) indicated that the reduction potential is governed by nucleophilic attack of electrons [56]. The reactivity of the present –N=N– center towards reduction was found to increase with the change of the substituent group attached to the benzene ring in the order: *m*-COOH (–I, –T) > *p*-SO$_3$H (–I) >*p*-CH$_3$ (+I, +T) since the $E_{1/2}$ values of the corresponding pyrazolyl-azo dyes I and III (*m*-COOH), II (*p*-SO$_3$H) and IV (*p*-CH$_3$) were –0.52, –0.64 and –0.73 V, respectively. It has also been shown that there is no effect on the reactivity of the –N=N– center towards reduction due to the substituent groups attached to the pyrazolyl ring of the investigated azo dye since no shift was observed in the $E_{1/2}$ value e.g. from compound (I) to compound (III) at the same pH value of 5, which meant that the reduction of −N=N− center was enhanced by the electron-withdrawing substituent attached to the benzene ring while it was retarded by the electron-repelling one. This behavior can be explained by the fact that the electron-withdrawing group reduces the basicity of the unprotonated nitrogen atom and consequently promote the reaction center. The effect of substituent groups on the reaction center is weak as realized from the small (ρ_π) value of 0.27 and since the substituent can affect the reaction center only by its inductive effect [56].

3.6. Spectrophotometric studies

The absorption spectra of the examined pyrazolyl-azo dyes (I–IV) were recorded within the wavelength range 200–600 nm in the B–R universal buffer of pH values 2–12 containing 10% (v/v) DMF. As a representative compound, the spectra of compound (IV) showed two absorption bands, the extinction of the band at longer wavelength ($\lambda_{max} = 400$ nm) decreased with the increase of pH while that of the shorter wavelength ($\lambda_{max} = 373$ nm) was much developed (e.g. Fig. 6). This behavior indicated that the 1st band at the shorter wavelength represents the absorption of species of the pyrazolyl-azo dye in which the phenolic OH-group is ionized, whereas the 2nd one at the longer wavelength represents the absorption of species of the pyrazolyl-azo dye in which the phenolic OH-group is non-ionized. An isosbestic point can be observed for the representative pyrazolyl-azo dye (IV) at $\lambda_{max} = 383$ nm within the pH range 8.9–12. This behavior indicated the presence of each of the investigated pyrazolyl-azo dyes in an acid–base equilibrium. The variation of absorbance with pH at the two wavelengths 373 and 400 nm are typical S and Z-shaped, respectively (e.g. Fig. 7a), which indicated the transformation of the molecule from one form into another. The absorbance–pH curves for the investigated pyrazolyl-azo dyes were made use for the determination of their acid ionization constant pK_a values, where the two curves of each of the investigated compounds intersected at a pH value which equals its pK_a value. The obtained pK_a values of the investigated pyrazolyl-azo dyes (I–IV) agree well with those obtained from the dc-polarographic studies (Table 1). Two other methods namely the half-height and the modified limiting absorbance [57] methods were applied to determine the pK_a values of the investigated pyrazolyl-azo dyes (e.g. Fig. 7a and b) and the obtained results are reported in Table 2.

Acknowledgement

The authors express their deep thanks to Dr. M. El-Borai, Professor of Organic Chemistry, Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt, for his great guidance and support during preparation of the examined pyrazolyl-azo compounds at his research laboratory.

References

[1] Fraga SMB, Goncalves MST, Moura JCVP, Rani K. Chromophoric azo reagents for amino acid and peptide labeling. European Journal of Organic Chemistry 2004;8:1750–60.

[2] Przeszlakowski S, Wydra H. Paper-chromatography of some sulfonated azo-dyes used as metallochromic reagents in liquid–liquid anion-exchange systems. Chromatographia 1982;15:301–4.

[3] Ashuto SH, Pandey ND, Mehrotra JK. Azo-dyes as metallochromic indicators. Colourage 1979;26:25.

[4] Sommer L, Koblizko V. Heterocyclic azo-dyes derived from 1-naphthol-4-sulphonic acid as metallochromic indicators. Collection of Czechoslovak Chemical Communications 1974;39:396–415.

[5] Woodward C, Freiser H. Sulphonated azo-dyes as extractive metallochromic reagents. Talanta 1973;20:417–20.

[6] Coelho PJ, Carvalho LM, Fonseca AMC, Raposo MMM. Photochromic properties of thienylpyrrole azo in solution. Tetrahedron Letters 2006;47:3711–4.

[7] Serwadczak M, Kucharski S. Photochromatic gratings in sol–gel hybrid materials containing cyanoazobenzene chromophores. Journal of Sol–Gel Science and Technology 2006;37:57–62.

[8] Dixit BC, Patel HM, Desai DJ. Synthesis and application of new mordent and disperse azo dyes based on 2,4-dihydroxybenzophenone. Journal of the Serbian Chemical Society 2007;72:119–27.

[9] Trofimov BA, Schmidt EY, Mikhaleva AI, Vasiltsov AM, Zaitsev AB, Smolyanina NS, et al. 2-Arylazo-1-vinylpyrroles: a novel promising family of reactive dyes. European Journal of Organic Chemistry 2006;17:4021–33.

[10] Khosravi A, Moradian S, Gharanjig K, Taromi FA. Investigation of synthesis and dyeing properties of some azonaphthalimide disperse dyestuffs for the dyeing of polyester fibers. Iranian Polymer Journal 2005;14:667–79.

[11] Patel KJ, Patel MP, Patel RG. Synthesis and studies of coloured polyesters derived from bis-azo diols. Indian Journal of Chemical Technology 2000;7:307–11.

[12] Peters AT, Bide MJ. Phenylazo derivatives of 1,8-naphthalimides and of 7*H*-benzimidazo(2,1-*a*)benz(*d*,*e*) isoquinolin-7-ones-dyes for synthetic-polymer fibers. Dyes and Pigments 1986;7:237–47.

[13] Choi JH, Hong SH, Towns AD. High fastness heterocyclic azo disperse dyes bearing ester function. Journal of the Society of Dyers and Colourists 1999;115:32–7.

[14] Towns AD. Development in azo disperse dyes derived from heterocyclic diazo components. Dyes and Pigments 1999;42:3–8.

[15] Hallas G, Towns AD. Dyes derived from aminothiophenes. 3. Application of some disperse dyes derived from 2-aminothiophenesto hydrophobic fibers. Dyes and Pigments 1997;33:215–28.

[16] Yin SC, Xu HY, Shi WF, Bao L, Gao YC, Song YL, et al. Preparation and optical properties of poly(4-ethynyl-4-[*N*,*N*-diethylamino]azobenzene-*co*-phenylacetylene). Dyes and Pigments 2007;72:119–23.

[17] Raposo MMM, Sousa AMRC, Fonseca AMC, Kirsch G. Thienylpyrrole azo dyes: synthesis, solvatochromic and electrochemical properties. Tetrahedron 2005;61:8249–56.

[18] Carella A, Centore R, Sirigu A, Tuzi A, Quatela A, Schutzmann S, et al. Second order non-linear optical performances of polymers containing imidazole and benzimidazole chromophores. Macromolecular Chemistry and Physics 2004;205:1948–54.

[19] Yesodha SK, Pillai CKS, Tsutsumi N. Stable polymeric materials for nonlinear optics: a review based on azobenzene systems. Progress in Polymer Science 2004;29:45–74.

[20] Birabassov R, Galstian TV. Light-induced macroscopic chirality in azo-dye-doped polymers. Journal of the Optical Society of America B: Optical Physics 2001;18:1469–73.

[21] Albu AM, Marculescu B, Ds Vasilescu. Synthesis and characterization of some polymers with application in non-linear optics. II. Copolymerization of styrene with some monomers containing azo-dyes. European Polymer Journal 1999;35:2203–5.

[22] Ruyffelaere F, Nardello V, Schmidt R, Aubry JM. Photosensitizing properties and reactivity of aryl azo naphtol dyes towards singlet oxygen. Journal of Photochemistry and Photobiology A: Chemistry 2006;183:98–105.

[23] El-Mekawi D, Abdel-Mottaleb MSA. The interaction and photostability of some xanthenes and selected azo sensitizing dyes with TiO_2 nanoparticles. International Journal of Photoenergy 2005;7:95–101.

[24] Ohlsson J, Wolpher H, Hagfeldt A, Grennberg H. New dyes for solar cells based on nanostructured semiconducting metal oxides: synthesis and characterization of ruthenium(II) complexes with thiol-substituted ligands. Journal of Photochemistry and Photobiology A: Chemistry 2002;148:41–8.

[25] Grafe A, Haupt K, Mohr GJ. Optical sensor materials for the detection of amines in organic solvents. Analytica Chimica Acta 2006;565: 42–7.

[26] Zhang DQ, Zhang M, Liu ZQ, Yu MX, Li Fy, Yi T, et al. Highly selective colorimetric sensor for cysteine and homocysteine based on azo derivatives. Tetrahedron Letters 2006;47:7093–6.

[27] Makedonski P, Brandes M, Grahn W, Kowalsky W, Wichern E, Wiese S, et al. Synthesis of new kinds of reactive azo dyes and their application for fiber-optical pH-measurements. Dyes and Pigments 2004;61:109–19.

[28] Mhor GJ, Citterio D, Demuth C, Fehimann M, Jenny L, Lohse C, et al. Reversible chemical reactions as the basis for optical sensors used to detect amines, alcohols and humidity. Journal of Materials Chemistry 1999;9:2259–64.

[29] Menek N, Karaman Y. Polarographic and voltammetric investigation of 6′-butoxy-2,6-diamino-3,3′-azodipyridine. Dyes and Pigments 2006;68: 101–8.

[30] Costea L, Bercean VN, Badea V, Chiriac A. Synthesis and electrochemical characteristics of dyes based upon 1*H*-3-phenyl-6-methyl-7-aril-azo-pyrazolo[5,1-*c*][1,2,4]triazole. Revista de Chimie 2006;57:71–4.

[31] Jayadevappa H, Shivaraj Y, Mahadevan KM, Kumaraswamy BE, Sathpathi AK, Sherigara BS. Electrochmical behavior of some industrially important azonaphthol derivatives at glassy carbon electrode. Indian Journal of Chemical Technology 2006;13:269–74.

[32] Menek N, Karaman Y. Polarographic and voltammetric investigation of 8-hydroxy-7-(4-sulfo-1-naphthylazo)-5-quinoline sulfonic acid. Dyes and Pigments 2005;67:9–14.

[33] Menek N, Basaran S, Turgut G, Odabsoglu M. Polarographic and voltammetric investigation of 3-allyl-4-hydroxyazobenzene. Dyes and Pigments 2004;61:85–91.

[34] Mandic Z, Nigovic B, Simunic B. The mechanism and kinetics of the electrochemical cleavage of azo bond of 2-hydroxy-5-sulfophenyl-azo-bebzoic acids. Electrochimica Acta 2004;49:607–15.

[35] De Paula FS, Cioletti AG, da Silva JF, Santana AEG, dos santos AF, Goulart MOF, et al. Electrochemical studies of biologically active arylazoxy compounds. The relationship between redox potentials and molluscicidal activities. Journal of Electroanalytical Chemistry 2003;544:25–34.

[36] Jain R, Bhargava M, Sharma N. Electrochemical studies on a pharmaceutical azo dye: Tartrazine. Industrial and Engineering Chemistry Research 2003;42:243–7.

[37] Ucar M, Solak AO, Menek N. Electrochemical behavior of 2-halogenated derivatives of *N*,*N*-dimethyl-4-aminoazobenzene at mercury electrode. Analytical Sciences 2002;18:997–1002.

[38] Peng X, Wang J. Electrochemical behavior of azo dyes in acid–ethanol media. Dyes and Pigments 1992;20:73–81.

[39] Killa HM, Mabrouk EM, El-Fattah AAA, Yasen SA. Electrochemical behavior of some azo-compounds of 4-aminoantipyrine derivatives using cyclic voltammetry and dc-polarography. Analytical Letters 1991;24:257–85.

[40] Fahmy HM, Helmy AMA, Abdel Azzem M. Polarographic behavior of dimedone-2-arylazo derivatives in alcoholic aqueous media. Journal of Electroanalytical Chemistry 1986;201:101–12.

[41] Ghoneim MM, Issa YM, Mabrouk EM, Amerah T. Polarographic reduction of phyenylazochromotropic acid dyes in aqueous buffer solutions at DME. Journal of the Electrochemical Society 1986;133:C133.

[42] Yaguez LID, Carrazon JMP, Diez LMP. Polarographic study of the 1-(2,4-dimethylphenylazo)-2-naphthol (Sudan-II) in hydroalcoholic medium. Electrochimica Acta 1986;31:119–21.

[43] Ning RY, Madan PB, Sternbach LH. Quinazolines and 1,4-benzodiazepines: syntheses of 7-acetyl-1,4-benzodiazepines. Journal of Heterocyclic Chemistry 1974;11:107–11.

[44] Song HF, Chen KC, Tian H. Synthesis of novel dyes derived from 1-ethyl-3-cyano-6-hydroxy-4-methyl-5-amino-2-pyridone. Dyes and Pigments 2002;53:257–62.

[45] El-Sayed HF. M.Sc. Thesis, Studies on some azo and azo methane dyes containing heterocyclic nucleus. Library of Faculty of Sci., Tanta Univ., Tanta, Egypt, private communication; 2005.

[46] Britton HTS. Hydrogen ions. 4th ed. London: Chapman & Hall; 1952. 113–114.

[47] Meites L. Polarographic techniques. 2nd.ed. New York: Interscience Publishers; 1965. 232–248.

[48] Zuman P. The elucidation of organic electrode process. New York: Academic Press; 1969. 20–51.

[49] Ghoneim MM, Ashy MAA. Polarographic reduction of phenolphthalein, cresolphthalein, thymolphthalein and α-naphtholphthalein in aqueous and nonaqueous ethanolic solutions. Canadian Journal of Chemistry 1979;57:1249–98.

[50] Kolthoff IM, Lingane JJ. Polarography, vol. 1. New York, London: Interscience Publishers; 1952. 43.

[51] Galus Z. In: Reynolds GF, editor. Fundamentals of electrochemical analysis. New York: John Wiley; 1976. p. 238.

[52] Nicholson RS, Shain I. Theory of stationary electrode polarography: single scan and cyclic methods applied to reversible, irreversible, and kinetic systems. Analytical Chemistry 1964;36:706–23.

[53] Bard AJ, Faulkner LR. Electrochemical methods: fundamentals and applications. New York: John Wiley & Sons; 1980. p. 218.

[54] Salem TM, Issa RM, Hindawey AM. Polarographic study of fluorescein in water-organic solvent. Annali di Chimica 1974;64:735–46.

[55] Hammett LP. Physical organic chemistry. New York: McGraw-Hill; 1940. p. 184.

[56] Zuman P. Substituent effects in organic polarography. New York: Plenum Press; 1967.

[57] Abdelhal FM, Issa RM, El-Ezabey MS, Hasanein AA. Spectral studies on fluorescein, eosin and erthrosin in solutions of varying pH values. Zeitschrift fur Physikalische Chemie – Frankfurt 1970;73:59–67.